The rotatory dispersion studies(3) : Stereochemistry of some derivatives of d-tartaric acid

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The Rotatory Dispersion Studies III.

Stereochemistry of Some Derivatives of *d*-Tartaric Acid

Koko SATSUMABAYASHI

Niigata Faculty, Nippon Dental College, No. 8, 1, Hamaura-cho, Niigata, Japan

Yojiro TSUZUKI, Shigeo TANAKA*, and Kazuyuki AOKI**

Department of Chemistry, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo

*Nippon Kayaku Company, Inc.
**Tokyo Metropolitan Government Office.

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旋光分散研究　第III報

d-酒石酸誘導体の立体化学

新潟歯学部　薩摩林紘子
東京理科大学理学部　都築洋次郎
田中茂夫
青木一幸

概　　要

前報で frexible conformation をもつ diacetyl *d*-tartaric acid の溶液中における preferable conformation を検討し，2つの staggered conformation が寄与することを述べた。

本報では，引き続き *d*-tartaric acid 誘導体の conformation を調べる。まず *d*-tartaric acid 誘導体のうち rigid conformation を有する単一5員環構造の anhydride についてその chirality を決定し，ついで frexible conformation を有する benzoate 誘導体に chirality rule を拡張して conformation に関する詳細な情報を求める。

単一5員環構造をもつ *d*-tartaric anhydride の dibenzoate 誘導体 (II, III) は符号の相反する2つの大きな Cotton 効果，すなわち，長波長側に正，短波長側に負の Cotton 効果を示した。これらは benzoate band の$\pi\rightarrow\pi^*$ transition の分裂によって生じたものであることを確認し，従って中西ら (Nakanishi *et al.*, *J. Am. Chem. Soc.*, **91**, 3989 (1969)) による dibenzoate chirality rule が適用可能で，それによると2つの benzoate group の間の chirality は正である。

さらに，この chirality rule が rigid な環状構造をもたない鎖状 dibenzoate (V-IX)

にも拡大して適用できることを確認し，それによって preferable conformation を推定した。その結果，これらの化合物では2つの dibenzoate group が負の chirality を有することが示されたが，その $[\theta]_{max}$ 値は benzoate 基のパラ位を NO_2, OCH_3, CH_3, Cl で置換した場合に期待される遷移モーメントの大きさに比例しない。このことから，実際の分子は chirality rule によって示された preferable conformation に対して他の conformer が平衡に寄与していると考えられる。さらに IR スペクトル測定の結果，分子内水素結合はカルボキシル基の C=O でなく，カルボキシル基の OH が関与していることを示し，2つの staggered conformation の存在を示唆し，OH 基が benzoate group の酸素原子に近く位置していることが示された。

The Rotatory Dispersion Studies III.[1]

Stereochemistry of Some Derivatives of *d*-Tartaric Acid

The conformation of several divenzoates of *d*-tartaric acid were investigated by means of optical rotatory dispersion. The dibenzoates of *d*-tartaric anhydride (II, III) with a five membered ring exhibited two strong Cotton effects of opposite sign, namely a positive effect in the longer wavelength region and a negative one in the shorter. These Cotton effects were found to be due to the splitting of the $\pi \rightarrow \pi^*$ transition of the benzoate bands, and the chirality was determined to be positive by applying the dibenzoate chirality rule.[2] Furthermore, it was found that this chirality rule can be applied to the acyclic dibenzoates (V-IX) which have no rigid conformations, and their preferred conformations were assigned based on the negative chirality of two benzoates groups. However, the $[\theta]_{max}$ values are not proportional to the magnitudes of the transition moments in the dibenzoated substituted with NO_2, OCH_3, CH_3, Cl groups in the para position. This fact suggests that the favorable conformation is in equilibrium with the other conformer. This conclusion was supported by the IR studies.

Tartaric acid is one of the classical substances most intensively studied since earliest times, being notorious for the complexity of its optical activity. Analysis of the RD curves of its cyclic derivatives, although in the visible region, enabled one of the authors[3] to assign the positive and negative partial rotations to the OH and COOH groups, respectively. The present

work is an extension of the stereochemical studies in ultraviolet region by various means and tartrates of flexible structure besides cyclic derivatives to confirm the predictions and also to interpret the results from recent viewpoints.

In the first place the RD of various diacyl derivatives of *d*-tartaric anhydride (I-III) was investigated and the CD as well as UV curves were measured in order to assign the Cotton effects. The results are shown in Figs. 2-4. It is seen that positive Cotton effects appear in all cases, and both the strength and the regions of the peaks are in the order: III>II>I. This fact is to be expected from an earlier RD investigation, which suggested that diacyl groups in the *d*-tartrates contribute to the positive rotation.[3]

On the other hand the phenomena conform also to the benzoate rule.

Although the benzoate chromophore has an intramolecular charge transfer band around 230 nm, due to the $\pi \rightarrow \pi^*$ transition, it has been reported with the dibenzoate derivatives of steroid glycols that the Cotton effects centred at 225 nm is splitted into two Cotton effects of opposite signs due to the dipole-dipole interaction between the electric transition moments of the two benzonate chromophores, and the sign of the Cotton effect at longer wavelength enables one to determine the chirality of the glycol.[2] Moreover, it was shown that this chirality method is applicable to other aromatic chromophores,[4] and can be used for determining the chirality of the diols of pyranose and furanose rings.[5] It is apparent that the cotton effects of the anhydrides of *d*-tartaric acid (II and III) conform to this chirality rule.

In a view of these facts we have performed RD and CD studies on diacyl derivatives of *d*-tartaric acid (IV-IX) in order to extend this chirality method to benzoates of the chain structure. Since the structures of these compounds are more or less liable to free rotation, the IR spectra were also obserbed to get more accurate informations on their conformations.

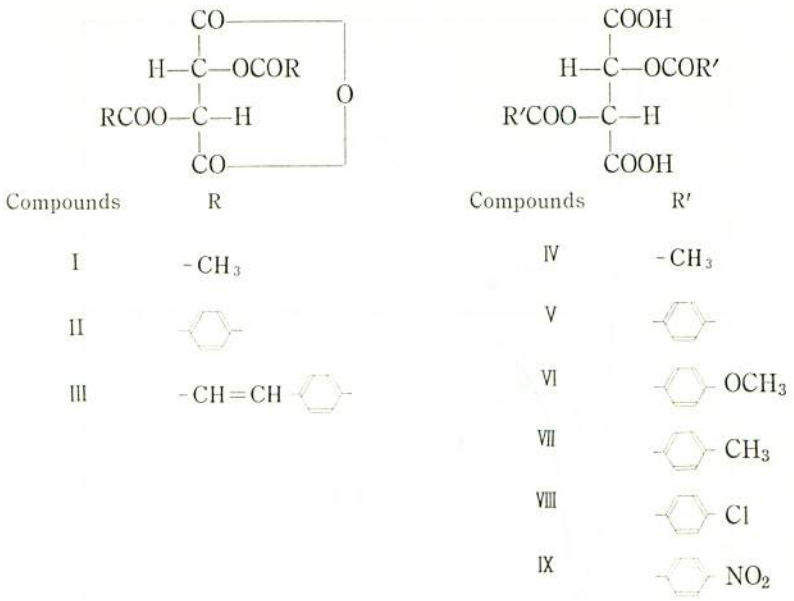

Fig. 1. Nine derivatives of *d*-tartaric acid.

Results and Discussion

In Fig. 2 are given the RD, CD and UV curves of diacetyl *d*-tartaric anhydride (Compound I). Compound I exhibits a weak absorption at 208 nm due to the $n \rightarrow \pi^*$ transition, which corresponds to the negative Cotton effect centred at 215 nm in the CD curve. By applying the lactone rule of planer five-membered ring[6] to the five-membered anhydride ring assumed as a sort of lactone, the oxygen atom attached to the asymmetric carbon atom enters into the negative octant, quite in conformity with the negative sign of the Cotton effect. Furthermore, it is shown that a negative Cotton effect is observed in Compound I, whose asymmetric carbon atoms are all of the R-configuration, as in the case of the five-membered sugar lactones.[7]

It should be noted that a small positive Cotton effect at 243 nm is due to the exciton band formed by the coupling of the carbonyl groups.[8]

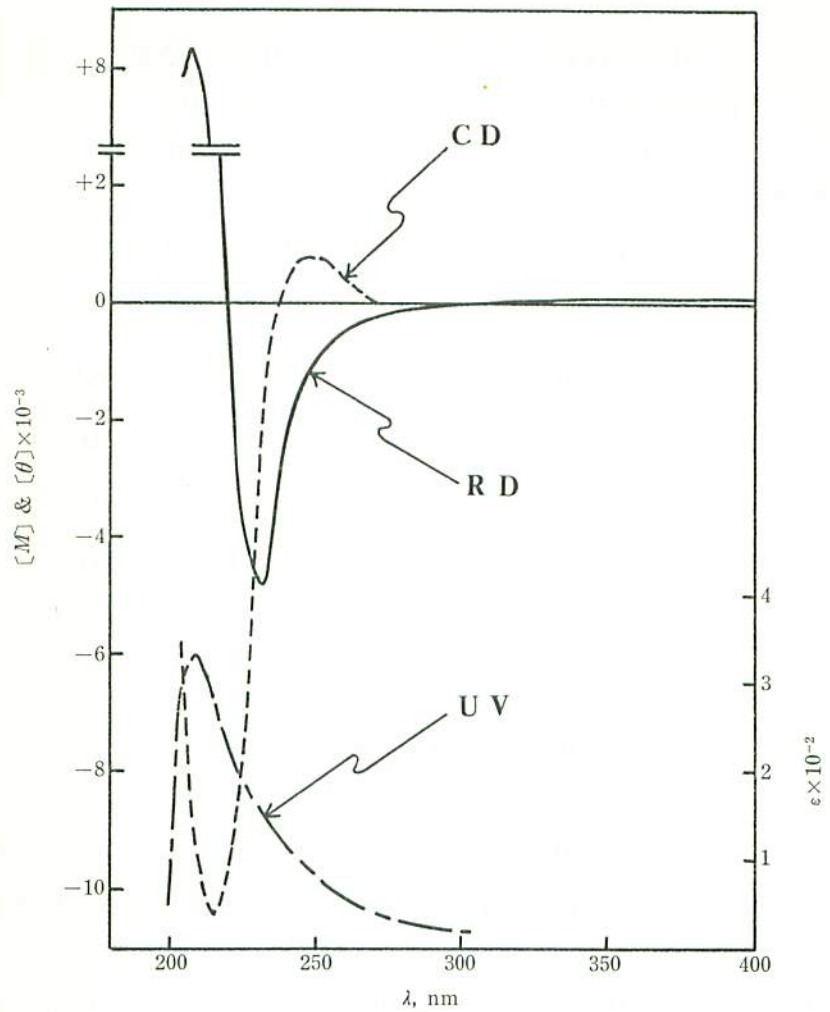

Fig. 2. RD, CD and UV of Compound I.

Fig. 3 and 4 give the RD, CD and UV spectra of dibenzoyl and dicinnamoyl derivatives of *d*-tartaric anhydride (Compounds II and III). The Cotton effect is splitted into two (positive and negative) due to the dipole-dipole interaction, since the $\pi \rightarrow \pi^*$ intramolecular charge transfer band of the benzoate groups becomes optically active. The absorption of the molecule is dominated by the $\pi \rightarrow \pi^*$ transition, since it is far stronger than the $n \rightarrow \pi^*$ transition. Hence, the dibenzoate chirality rule[2,4,5] is applicable to the compounds II

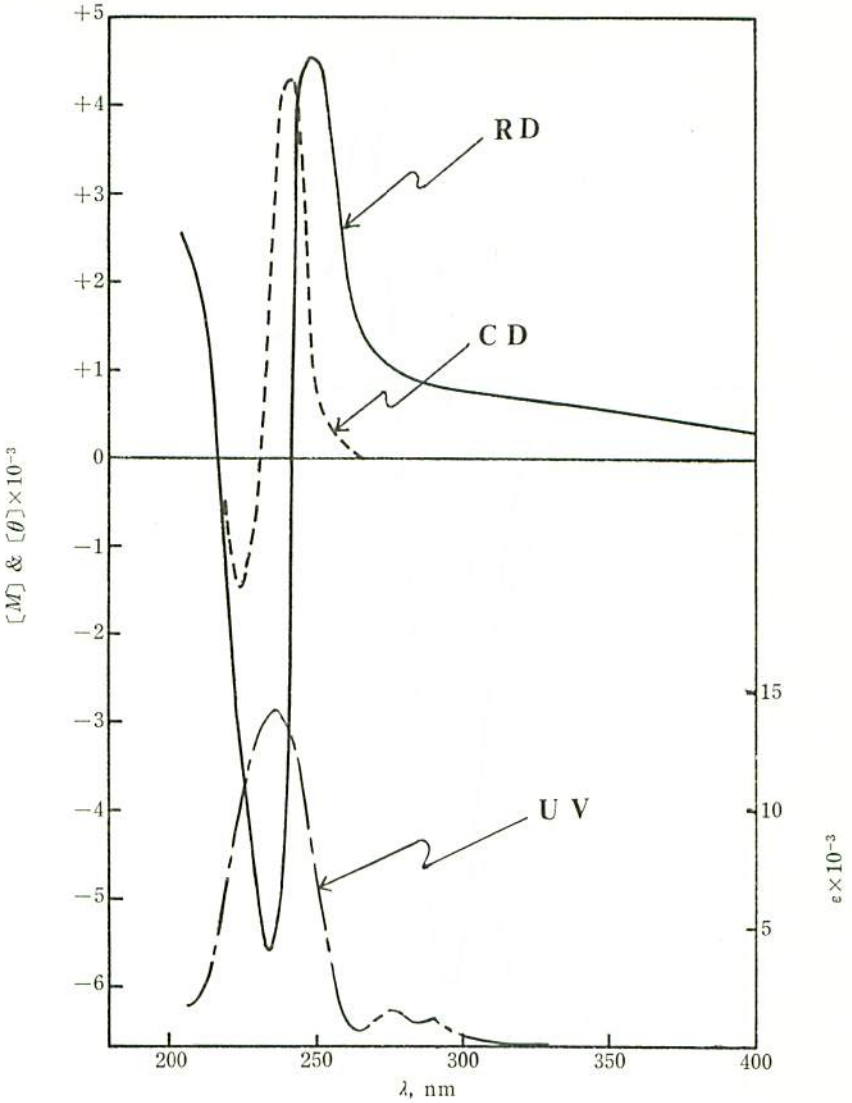

Fig. 3. RD, CD and UV of Compound II.

and III, while the lactone rule holds for the compound I. The positive first Cotton effect of these compounds indicates that they have the conformation of a positive chirality, as shown in Fig. 5.

As seen in Figs. 3 and 4 the CD curve of II showed a peak at 248 nm and a trough at 224 nm, but a red-shift of the Cotton effects in III is observed, far

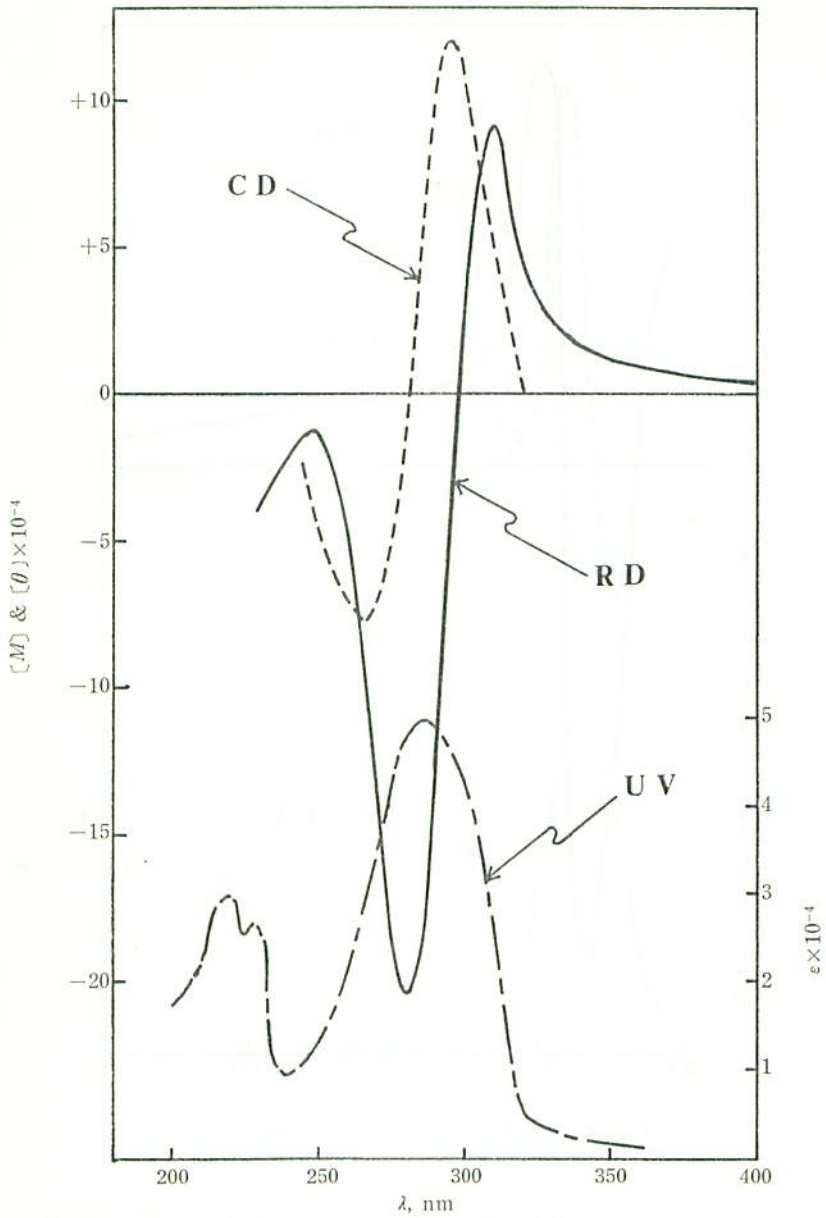

Fig. 4. RD, CD and UV of Compound III.

greater than those of ordinary benzoyloxy compounds. This is due to the conjugate system being more extended than the benzoyloxy group, with a larger transition moment. Thus a greater rotational contribution is expected

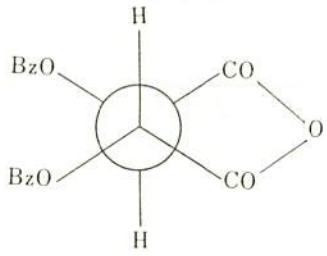

Fig. 5. Conformation of II (Bz=benzoyl group).

Table 1. The characteristic values of RD and CD of I-III

Comp.	RD				CD			
	Trough		Peak		Negative Max.		Positive Max.	
	λ(nm)	($[M]\times10^{-3}$)	λ(nm)	($[M]\times10^{-3}$)	λ(nm)	($[\theta]\times10^{-3}$)	λ(nm)	($[\theta]\times10^{-3}$)
I	230	(−4.79)	—	—	215	(−10.5)	243	(+0.72)
II	233	(−55.3)	248	(+45.2)	224	(−14.1)	244	(+42.3)
III	280	(−20.2)	309	(+90.4)	265	(−76.5)	296	(+120)

for this system.

In fact, the $[\theta]_{max}$ value of III is greater than that of II (Table 1) in harmony with the magnitude of the transition moment. However, strictly speaking, it is desirable to take into consideration the difference of symmetry between the chromophores of the cinnamate and the benzoate in the compounds II and III.

It is, therefore, evident that the dibenzoate chirality method is applicable to the anhydride ring as in the case of furanose ring,[5] thus enabling the conformation to be determined, though qualitatively, by RD studies.

The RD, CD and UV curves of diacetyl *d*-tartaric acid (Compound IV) are shown in Fig. 6. In accordance with the earlier prediction that the carboxyl group of *d*-tartaric acid contributes to negative rotation,[3] a unique negative Cotton effect appears in the RD and CD spectra attributable to the weak $n\rightarrow\pi^*$ transition of the carboxyl groups. Since no interaction between the carbonyl groups occurs, the molecule may adopt one of the two possible

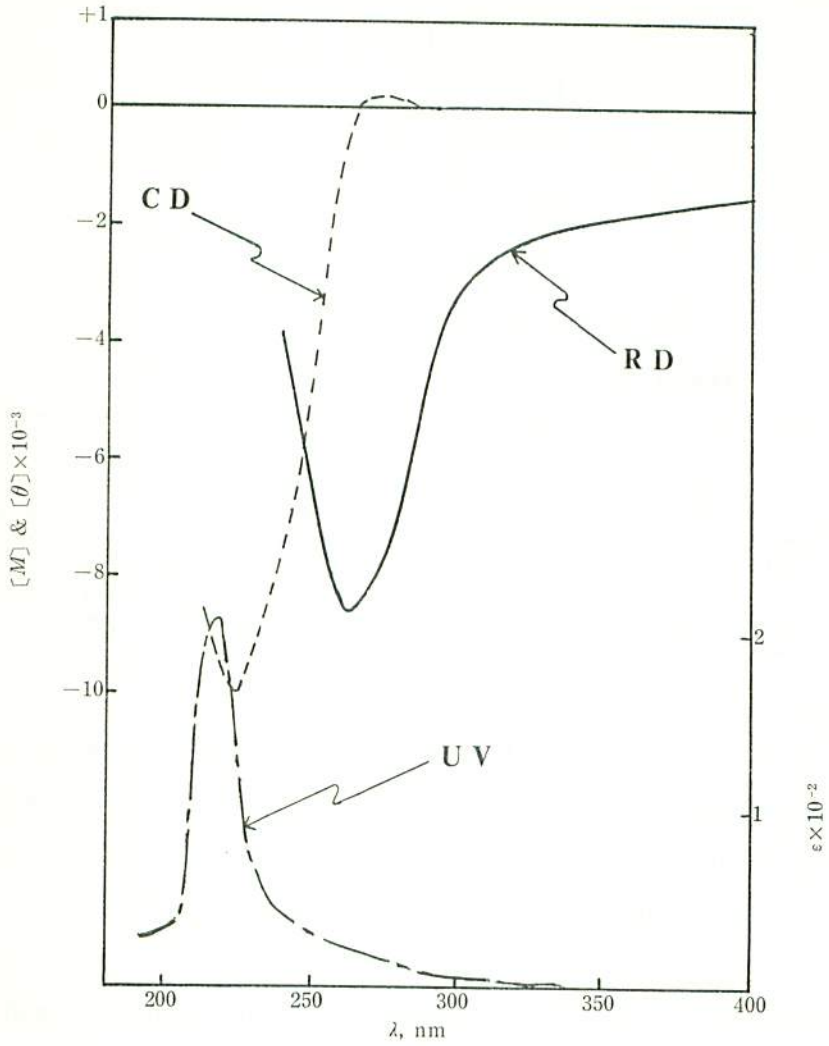

Fig. 6. RD, CD and UV of Compound IV.

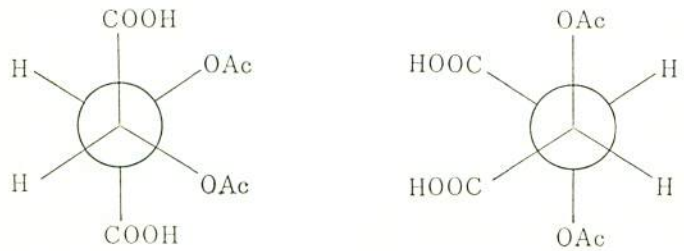

Fig. 7. Possible conformations of IV.

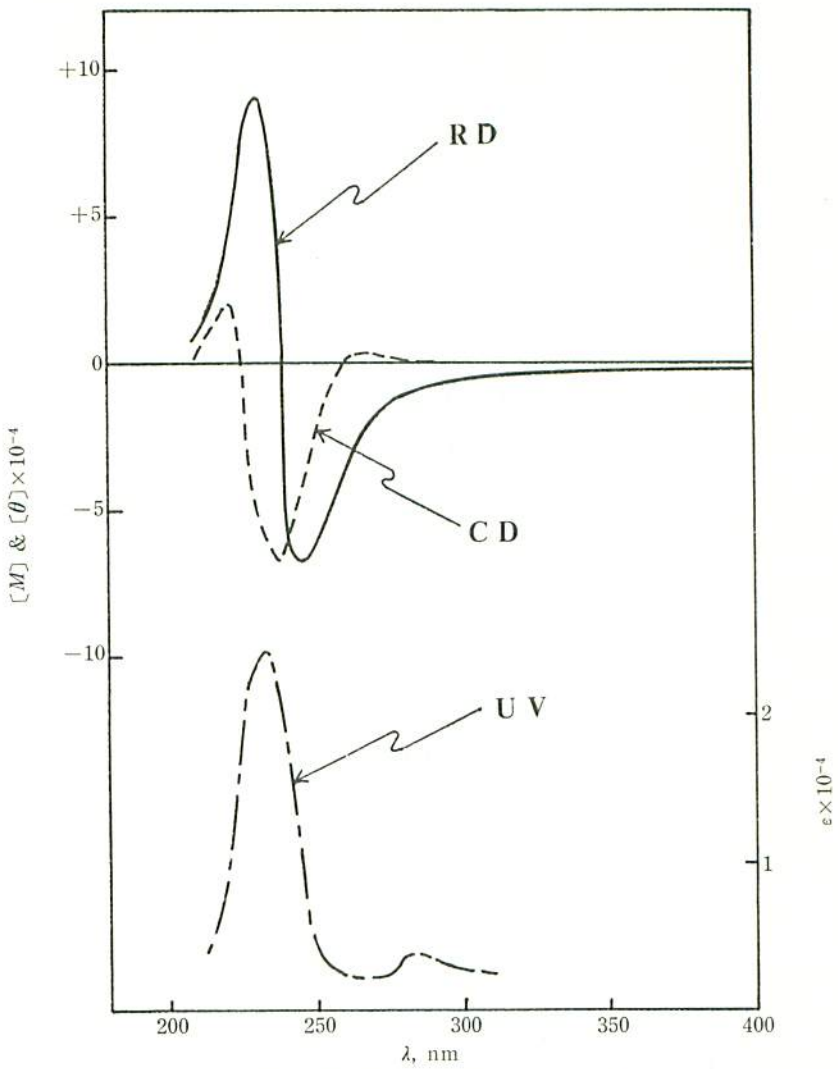

Fig. 8. RD, CD and UV of Compound V.

conformations (shown in Fig. 7), where either two carboxyl groups or two acetoxy groups are trans.

In order to get more accurate informations on the conformation, we have studied benzoyl and various *p*-substituted benzoyl *d*-tartaric acids (Compound V–IX). The RD, CD and UV spectra of dibenzoyl *d*-tartaric acid (Compound V) are presented in Fig. 8 as an example. These diacyl derivatives of

Table 2. The characteristic values of RD, CD and UV of IV–IX

Comp.	RD				CD				UV_{max}	
	Peak		Trough		Positive Max.		Negative Max.			
	λ(nm)	($[M]\times10^{-3}$)	λ(nm)	($[M]\times10^{-3}$)	λ(nm)	($[\theta]\times10^{-3}$)	λ(nm)	($[\theta]\times10^{-3}$)	λ(nm)	($\varepsilon\times10^{-4}$)
IV	—	—	232	(−8.7)	272	(+0.9)	222	(−10.0)	218	(0.02)
V	231	(+89.5)	245	(−66.7)	220	(+19.8)	238	(−66.8)	232	(2.42)
VI	257	(+16.9)	278	(−7.5)	226	(+3.1)	266	(−11.0)	258	(5.63)
VII	242	(+76.8)	257	(−67.2)	233	(+15.8)	250	(−94.7)	245	(4.14)
VIII	243	(+48.5)	258	(−63.1)	236	(+19.2)	252	(−72.1)	244	(3.91)
IX	258	(+22.2)	282	(−12.9)	245	(+5.8)	272	(−16.8)	261	(3.62)

d–tartaric acid exhibit, without exception, negative Cotton effets in the longer-wavelength region, but positive ones in the shorter-wavelength side. In Table 2 are summarized the characteristic values of the Cotton effects of IV–IX.

In Compound V with no substituent in the para position, the UV_{max} appears near 232 nm ($\varepsilon_{max}=24200$) and 280 nm ($\varepsilon_{max}=1940$), and the former absorption band due to the $\pi\rightarrow\pi^*$ intramolecular charge transfer of the benzoate chromophore is optically active. In the UV spectra of the compound (VI–IX) with *p*–substituted benzoate groups, red-shifts due to the *p*–substitution were observed, and it is evident that the optically active absorption bands of the Compounds V–IX are due to the $\pi\rightarrow\pi^*$ intramolecular charge transfer bands of the benzoate chromophores.[9] Since the UV_{max} lies nearly in the middle of the positive maximum and negative maximum of the CD curve in every case (Table 2), it is clear that the $\pi\rightarrow\pi^*$ intramolecular charge transfer bands of the para-substituted benzoates V–IX become optically active and are each splitted into two Cotton effects of opposite signs as in the case of compounds II and III. Thus the chirality method is applicable to aliphatic dibenzoates. Three sttaggered conformations are possible for compounds V–IX as is shown in Fig. 9.

Since the signs of the first Cotton effects of these compounds are all negative, the preferred conformer should have a negative chirality between the

benzoate groups. Therefore, the conformer A, being a negative chirality is considered to be favorable for them, because the conformer B has no chirality, and the former C, a positive chirality (Fig. 9).

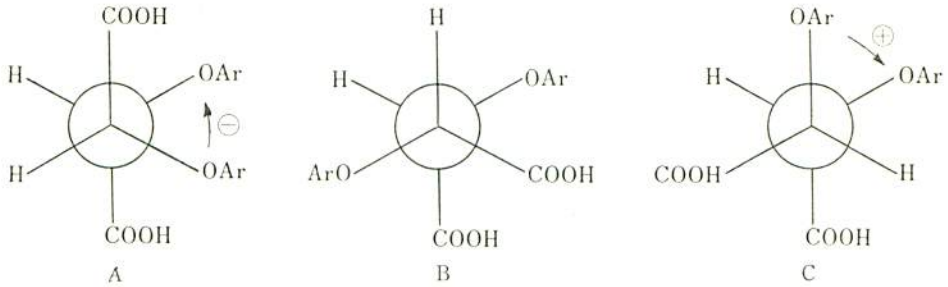

Fig. 9. Staggered conformeres of diacyl *d*-tartaric acid (Ar=benzoyl or *p*-substituted benzoyl).

In Table 3 were shown that the two higher frequencies due to the carbonyl groups of the benzoate compounds (V–IX). The wave numbers coincide with each other in both series within $\pm 2\,cm^{-1}$, showing that they are independent of the σ-values[10] of Hammett. In view of the fact that the high frequency of $\nu_{C=O}$ (above $1760\,cm^{-1}$), this band is considered to be attributed to the carboxyl CO group with no hydrogen bonding. The bands below $1760\,cm^{-1}$ are irregular and difficult to assign.

Table 3. The frequencies of the benzoates

Compounds	Benzo Groups	Wave Numbers (cm^{-1})
V		1782, 1764
VI	 OCH_3	1782, 1768
VII	CH_3	1783, 1765
VIII	 Cl	1784, 1765
IX	 NO_2	1782, 1768

The IR spectra show that a strong, broad band 3520 cm^{-1} due to the intramolecularly bonded OH group and a very weak band is observed at 3700 cm^{-1} due to the free OH group. The latter phenomenon demonstrates that the carboxyl OH group takes part in hydrogen bonding. Since each of the compounds (V–IX) similarly exhibits 3520 cm^{-1} and 3700 cm^{-1} bands due to the OH group, we have come to the conclusion that the intramolecular hydrogen bond of the carboxyl OH groups is accepted by the oxygen atom of the ester group. Therefore, the conformers A and B (Fig. 9) may be possible for this hydrogen bonding.

It has already been stated that the favorable conformer should be conformer A with a negative chirality. However, view of the possibility of hydrogen bonding and the irregularity of $[\theta]_{max}$ value against the ε_{max} value it is considered that conformer B also contributes to the following equilibrium, as shown in Fig. 10.

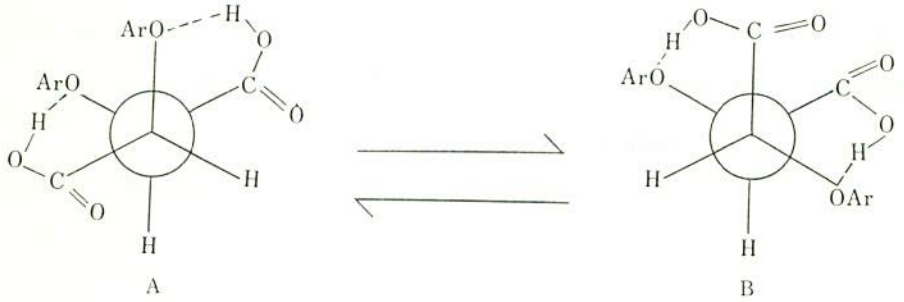

Fig. 10. Two possible conformations in equilibrium

(Ar = -CO⟨⬡⟩ or -CO⟨⬡⟩X)

In general, compounds with strong transition moment are expected to be stronger in rotatory contribution than those with weak transition moments, so that the compounds VI and IX should exhibit stronger Cotton effects than the compounds V, VII and VIII. But, as shown in Table 2, the compounds

VI and IX unexpectedly exhibit smaller Cotton effects than V. This fact suggests that the equilibrium is more shifted to conformer B in the compounds VI and IX as compared with V, VII and VIII. Hence conformer B must make a more or less contribution to the equilibrium with the conformer A, which is supported by the chirality rule as the favorable conformer.

Experimental

The samples were prepared according to the methods described in the literature with a slight modification. The rotatory dispersion and the circular dichroism were measured in dioxane (with compounds I–III) and 1, 2-dichloroethane (with compounds IV–IX) at 25°C in the wavelength region from 210 to 600 nm with a JASCO optical rotatory dispersion recorder of the ORD/UV-5 type. The UV absorption was measured in dioxane (with compounds I–III) and 1, 2-dichloroethane (with compounds IV–IX) with a self-recording spectrophotometer of Hitachi ESP-3T type. The IR specta were observed in chloroform and tetrachloroethlene below the concentration 1×10^{-3} mole/l with a grating infrared spectrometer, Model DS-403 G of the Japan Spectroscopic Co.

Diacetyl d-tartaric anhydride (Compound I). — Colorless needles; mp 135.0 –136.0 °C. The RD and CD were measured at 25 °C (*c* 0.194). $[\alpha]_{400}$ +10.3°, $[\alpha]_{230}$ −2220° (trough), $[\alpha]_{210}$ −1950°, $[\theta]_{270}$ 0°, $[\theta]_{243}$ +720° (peak), $[\theta]_{215}$ −10500° (trough), $[\theta]_{202}$ −6680°. UV (24 °C): ε_{max} 330 at 208 nm.

Dibenzoyl d-tartaric anhydride (Compound II). — Colorless needles; mp 174 °C. The RD and CD were measured at 25 °C (*c* 0.049): $[\alpha]_{589}$ +296°, $[\alpha]_{300}$ +3470°, $[\alpha]_{248}$ +13300° (peak), $[\alpha]_{233}$ −16300° (trough), $[\alpha]_{205}$ +7930°, $[\theta]_{265}$ 0°, $[\theta]_{242}$ +42300° (peak), $[\theta]_{224}$ −14100° (trough), $[\theta]_{220}$ −6630°. UV (20.5 °C): ε_{max} 14200 at 236 nm, ε_{max} 1430 at 276 nm and ε_{max} 1210 at 288 nm.

Dicinnamoyl d-tartaric anhydride (Compound III). — Colorless needles; mp 163–164 °C. The RD and CD were measured at 25 °C (*c* 0.075) : $[\alpha]_{589}$ +1060°, $[\alpha]_{400}$ +5070°, $[\alpha]_{309}$ +90400° (peak), $[\alpha]_{280}$ −202000° (trough), $[\alpha]_{230}$ −38300°, $[\theta]_{321}$ 0°, $[\theta]_{296}$ +119000° (peak), $[\theta]_{265}$ −76500° (trough), $[\theta]_{240}$ 0°. UV (24 °C) : ε_{max} 29400 at 219 nm, ε_{max} 26600 at 225 nm and ε_{max} 46900 at 286 nm.

Diacetyl d-tartaric acid (Compound IV). — Colorless needles; mp 118–119 °C. The RD and CD were measured at 25 °C (*c* 0.049) : $[\alpha]_{600}$ −39.5°, $[\alpha]_{589}$ −40.8, $[\alpha]_{232}$ −3710° (trough), $[\alpha]_{220}$ −1630°. $[\alpha]_{207}$ +3550°, $[\theta]_{280}$ 0°, $[\theta]_{272}$ +90.0° (peak), $[\theta]_{222}$ −10100° (trough), $[\theta]_{212}$ −9450°. UV (20 °C) : ε_{max} 208 at 218 nm.

Dibenzoyl d-tartaric acid (Compound V). — Colorless needles; mp 138–139 °C. The RD and CD were measured at 25 °C (*c* 0.110) : $[\alpha]_{600}$ −127°, $[\alpha]_{589}$ −130°, $[\alpha]_{245}$ −18600° (trough), $[\alpha]_{231}$ +25000° (peak), $[\alpha]_{210}$ +2270°, $[\theta]_{260}$ 0°, $[\theta]_{237}$ −66700° (trough), $[\theta]_{220}$ +19800° (peak), $[\theta]_{210}$ +2470°. UV (25 °C) : ε_{max} 24200 at 232 nm, ε_{max} 1940 at 270 nm and ε_{max} 1550 at 283 nm.

Dianisoyl d-tartaric acid (Compound VI). — Colorless needles; mp 180–181 °C. The RD and CD were measured at 25 °C (*c* 0.113) : $[\alpha]_{600}$ −26.5°, $[\alpha]_{589}$ −27.0°, $[\alpha]_{278}$ −1790° (trough), $[\alpha]_{257}$ +4040° (peak), $[\alpha]_{240}$ +448°, $[\theta]_{280}$ 0°, $[\theta]_{266}$ −11000° (trough), $[\theta]_{226}$ +3050° (peak), $[\theta]_{220}$ −6100°. UV (25 °C) : ε_{max} 56300 at 258 nm, ε_{max} 28500 at 274 nm and ε_{max} 8710 at 283 nm.

Ditoluyl d-tartaric acid (Compound VII). — Colorless needles; mp 172 °C (decomp.). The RD and CD were measured at 25 °C (*c* 0.091) : $[\alpha]_{600}$ −128°, $[\alpha]_{589}$ −138°, $[\alpha]_{257}$ −17400° (trough), $[\alpha]_{242}$ +19900° (peak), $[\alpha]_{214}$ +4590°, $[\theta]_{295}$ 0°, $[\theta]_{250}$ −94900° (trough), $[\theta]_{233}$ +15800° (peak), $[\theta]_{215}$ −22500°. UV (25°C) : ε_{max} 41400 at 245 nm, ε_{max} 2890 at 272 nm and ε_{max} 1700 at 283 nm.

Di-p-chlorobenzoyl d-tartaric acid (Compound VIII). — Colorless needles; mp 178–179 °C. The RD and CD were measured at 25 °C (*c* 0.088) : $[\alpha]_{600}$ −128°, $[\alpha]_{589}$ −136°, $[\alpha]_{258}$ −14800° (trough), $[\alpha]_{243}$ +11400° (peak), $[\alpha]_{210}$ −3410°, $[\theta]_{278}$ 0°, $[\theta]_{252}$ −72100° (trough), $[\theta]_{236}$ +19200° (peak), $[\theta]_{210}$ −35200°. UV (25 °C) :

ε_{max} 39100 at 244 nm, ε_{max} 6620 at 274 nm and ε_{max} 5500 at 283 nm.

Di-p-nitrobenzoyl d-tartaric acid (Compound IX). — Yellowish needles; mp 188–189 °C. The RD and CD were measured at 25 °C (*c* 0.110) : $[\alpha]_{600}$ −49.0°, $[\alpha]_{589}$ −59.0°, $[\alpha]_{282}$ −2880° (trough), $[\alpha]_{258}$ +4960° (peak), $[\alpha]_{220}$ +1180°, $[\theta]_{310}$ 0°, $[\theta]_{272}$ −16800° (trough), $[\theta]_{245}$ +5800° (peak), $[\theta]_{227}$ 0°. UV (25 °C) : ε_{max} 36200 at 261 nm.

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